

ENERGY INNOVATIONS SMALL GRANT PROGRAM Renewable Energy Technologies

Non-Vacuum Thin-Film Photovoltaics Processes

FEASIBILITY ANALYSIS

March 2003 P500-03-019F



Gray Davis, Governor

CALIFORNIA ENERGY COMMISSION

Prepared By: Hal Clark

Grant Program Administrator

San Diego State University Foundation

Prepared For:California Energy Commission Energy Innovations Small Grant Program

Researcher: Chris Eberspacher Unisun

Grant Number:

99-31

Philip Misemer

Grant Program Manager

Marwan Masri

Deputy Director

Technology Systems Division

Robert Therkelsen

Executive Director

LEGAL NOTICE

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the state of California. The Commission, the state of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to \$75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
 - o Appendix A: Final Report (under separate cover)
 - o Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at: http://www.energy.ca.gov/research/innovations

or contact the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at http://www.energy.ca.gov/research/index.html.

Executive Summary

Introduction

Photovoltaics (PV) is a small but rapidly growing sector of California's electrical power generation capacity. For PV to significantly impact the State's economy and quality of life, the cost of PV-generated power must decrease. One of the most promising strategies for lowering PV costs is the use of technologies in which thin films of materials are deposited on inexpensive substrates like window glass. One of the most promising thin-film materials is copper indium gallium selenide (CuIn_{1-x}Ga_xSe₂ or CIGS).

Vacuum deposition processes have difficulty depositing CIGS films on large areas with the precision and control necessary to achieve low manufacturing costs. Non-vacuum deposition techniques provide a simple, low-cost alternative. Preparing fine powders of precursor materials, depositing thin layers of the particulate precursor materials, and sintering the layers into high-quality dense films can form high quality thin films.

Simple, non-vacuum techniques such as spraying and printing can deposit layers of particles on large-area substrates. Exploratory materials research using simple pneumatic spraying yielded cells with 11.7% efficiencies and monolithic multi-cell modules with 5% efficiencies. However, the sprayed layers were not very planar (i.e. flat) and were not very well packed (i.e. dense), and deposition rates and materials use efficiency were low. The aim of this EISG project was to deposit uniform, planar, well-packed layers with high materials use efficiency (MUE).

Objectives

The goal of this project was to determine the feasibility of depositing planar, well-packed particulate layers at high rates with high materials use efficiency (MUE) using non-vacuum techniques. The researcher established the following project objectives:

- 1. Identify high-MUE, non-vacuum deposition techniques and obtain suitable equipment for experimental evaluation
- 2. Develop high-MUE spraying techniques using CIGS precursor materials
- 3. Fabricate efficient thin-film PV devices using high-MUE techniques.

Outcomes

- 1. The researcher identified high-MUE, non-vacuum deposition techniques and procured suitable equipment for experimental evaluation.
 - Pneumatic spraying resulted in good atomization and excellent spray directionality, but materials use efficiency was low.
 - Without gas assistance, ultrasonic spraying resulted in good atomization, but the lack of carrier gas resulted in poor spray directionality.
 - Gas-assisted ultrasonic spraying yielded good atomization and good spray directionality.
 - Electrostatic spraying at 30 kV yielded relative materials use efficiency gains of 50-65%, but the deposition pattern was erratic and irreproducible.

- Casting and spray casting yielded high materials use efficiencies and well-packed, planar layers.
- 2. The researcher developed high-MUE deposition techniques for depositing layers of CIGS precursor particulate materials.
 - The morphology of particle layers deposited by pneumatic spraying varied with spraying conditions.
 - Layers sprayed in a manner that facilitated rapid local solvent evaporation exhibited microscopically planar surfaces.
 - Layers sprayed using slow solvent evaporation conditions exhibited non-planar surfaces characterized by a network of ridges and valleys.
 - Droplet drying mechanisms resulted in observed morphological variations.
 - Individual droplets of well-dispersed, well-suspended slurry dried to form rings of particles.
 - Networks of ridges and valleys evolved as particles were differentially collected into ridges by the interplay of ring overlap, particle bounce-back, high-angle over spray, and particle/gas lateral flow.
 - Spray conditions that facilitate rapid solvent drying mitigated local drying effects that
 cause non-planar layer morphologies; but such conditions reduced materials use
 efficiency.
 - Ultrasonic spraying minimized particle loss mechanisms and yielded higher materials use efficiencies; however, ultrasonic spray deposition resulted in non-planar layers characterized by ridges, valleys, and small agglomerates.
 - Spraying under conditions that mitigate in-flight droplet drying sharply reduced the density of small agglomerates; but slow-evaporation conditions aggravated the tendency to form a ridges and valleys topology.
 - Casting techniques, which use a continuous "wet film" of slurry rather than isolated droplets, circumvented the non-planar morphologies that result from cycles of wetting and drying.
 - The substrate-wide drying front inherent to solvent evaporation from continuous wet films minimized the formation of ridges and valleys.
- 3. The researcher fabricated thin-film PV devices using particulate precursor materials deposited using high-MUE techniques, achieving cell efficiencies of 9.4%.

Conclusions

- 1. The results demonstrate high-MUE deposition processes can yield PV devices with the efficiencies needed to fabricate commercially viable products.
- 2. Cost-effective formation of high-quality PV films using particle-based, non-vacuum processes requires the deposition of reasonably planar, well-packed layers of particulate precursor materials with high materials use efficiencies.

- 3. Non-vacuum spraying techniques provide the necessary combination of planar, well-packed layers and efficient materials use provided one mitigates nozzle-related agglomeration, avoids repeated wetting/drying that can cause non-planar morphologies, and facilitates particle rearrangement that can increase packing densities. The demonstration of efficient spray deposition of planar, well-packed layers lays the foundation for the fabrication of efficient, large-area, thin-film PV modules using non-vacuum processes.
- 4. Since the techniques developed in this project can yield higher particle packing densities in particulate precursor layers, improvements to final film quality can accrue from adjustments to the reactive sintering processes used to convert porous precursor layers into dense final films.

Benefits to California

If this line of research reaches a successful conclusion, California will benefit in several ways. Rooftops equipped with solar power systems provide customers the option of generating their own clean, quiet, reliable electricity. Solar power, with its ability to provide electricity at home or at a business site, can help offset the need to purchase electricity and increase consumer autonomy. PV technologies based on thin films can potentially deliver the end-user price reductions necessary to expand the use of PV significantly and aid California ratepayers in realizing a pollution-free, renewable energy option.

Recommendations

The techniques developed in this project yield efficient small-area solar cells. Further research is needed to test these techniques in the fabrication of larger-area, monolithically integrated, multicell modules suitable for commercial production. The next steps are:

- Investigate synergies that might arise from combining improved particle layer deposition techniques with improvements to the layer-to-film sintering processes
- Apply the high-MUE particulate layer deposition techniques to the fabrication of largearea, multi-cell modules.

.

Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project's level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

Development Stage/Activity Matrix

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: http://www.energy.ca.gov/research/innovations and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

	Development Stages:		Development Activities:
Stage 1:	Idea Generation & Work	Activity 1:	Marketing / Connection to Market
	Statement Development	Activity 2:	Engineering / Technical
Stage 2:	Technical and Market Analysis	Activity 3:	Legal / Contractual
Stage 3:	Research & Bench Scale Testing	Activity 4:	Environmental, Safety, and Other
Stage 4:	Technology Development and		Risk Assessments / Quality Plans
	Field Experiments	Activity 5:	Strategic Planning / PIER Fit -
Stage 5:	Product Development and Field		Critical Path Analysis
	Testing	Activity 6:	Production Readiness /
Stage 6:	Demonstration and Full-Scale		Commercialization
	Testing	Activity 7:	Public Benefits / Cost
Stage 7:	Market Transformation		
Stage 8:	Commercialization		

Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

Development Assessment Matrix

Stages Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research		l	4 Technology Develop- ment	5 Product Develop- ment	6 Demon- stration	7 Market Transfor- mation	8 Commer- cialization
Marketing										
Engineering / Technical										
Legal/ Contractual										
Risk Assess/ Quality Plans										
Strategic										
Production. Readiness/										
Public Benefits/ Cost										

The Program Administrator's assessment was based on the following supporting details:

Marketing/Connection to the Market.

The researcher has not submitted a preliminary business plan at this time. Potential commercializers should be contacted and interviewed to provide feedback from currently identified potential customers as well as to identify additional customers and stakeholders.

Engineering/Technical.

Each method that was tested was unable to achieve all goals. Future work will involve incorporating two or more processes to achieve the stated goals.

Legal/Contractual.

Prior to this project, the researcher defined intellectual property, reviewed prior art, submitted patent applications, and assessed technology-licensing requirements. During this EISG project he received notice of allowance for the first patent. No contractual agreements have been made.

Environmental, Safety, Risk Assessments/ Quality Plans.

Initial drafts of the following Quality Plans are needed prior to initiation of Stage 4 development activity: Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety.

Strategic.

This product has no known critical dependencies on other projects under development by PIER or elsewhere.

Production Readiness/Commercialization.

No commercialization partner has been selected.

Public Benefits/Costs.

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system.
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

Photovoltaic systems reduce environmental impacts of the California electricity supply or transmission or distribution system. This project potentially reduces the cost to manufacture PV cells and modules. Lower cost modules will lead to lower cost PV generation systems. Cost effective PV systems will increase the application of this technology and thus reduce the environmental impact of electric generation in California.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

Appendix A to FAR 99-31

ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

(EISG) FINAL REPORT

NON-VACUUM THIN-FILM PHOTOVOLTAICS PROCESSES

EISG AWARDEE

Unisun
587-E North Ventu Park Road, PMB 124
Newbury Park, CA 91320
Phone: (805) 987-7258
Email: unisun@aol.com

AUTHORS

Chris Eberspacher, Principal Investigator Karen Pauls, Senior Research Engineer Jack Serra, Senior Research Engineer

> Grant #: 99-31 Grant Funding: \$75,000

Term: August 15, 2000 – June 15, 2001 PIER Subject Area: Renewable Energy Technologies

Legal Notice

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the State of California. The Commission, the State of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

Acknowledgements

We are indebted to Jie Zhu and Udai Singh of the Institute of Energy Conversion (IEC) at the University of Delaware for materials analyses, to Bob Gay of Siemens Solar Industries for Mo-coated glass, and to Alan Fahrenbruch of Stanford University, Bob Birkmire and Bill Shafarman of IEC, and Dave Ginley of the National Renewable Energy Laboratory for discussions on materials processing strategies and equipment design.

Table of Contents

PREFACE	1
EXECUTIVE SUMMARY	2
ABSTRACT	5
INTRODUCTION	6
PROJECT APPROACH	10
PROJECT OUTCOMES	11
CONCLUSIONS AND RECOMMENDATIONS	17
DEVELOPMENT STAGE ASSESSMENT	19
REFERENCES	
GLOSSARY	22
LIST OF FIGURES	23
LIST OF TABLES	23

Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program. The EISG Program awards grants up to \$75,000 for promising public interest energy research that is in the proof-of-concept stage of development.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research.

For more information on the EISG Program, please visit the Commission's Web site at: http://www.energy.ca.gov/research/innovations/index.html.

For more information on the overall PIER Program, please visit the Commission's Web site at: http://energy.ca.gov/research/index.html.

Inquires related to this final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

Executive Summary

Introduction

Photovoltaics (PV) is a small but rapidly growing sector of California's electrical power generation capacity. In order for PV to significantly impact the State's economy and quality of life, the cost of PV-generated power must decrease. One of the most promising strategies for lowering PV costs is the use of thin-film technologies in which thin films of materials are deposited on inexpensive large-area substrates like window glass. One of the most promising thin-film materials is copper indium gallium selenide ($Culn_{1-x}Ga_xSe_2$ or CIGS).

CIGS films are generally deposited by vacuum-deposition processes, but it is difficult to deposit films on large areas with the precision and control necessary to achieve low manufacturing costs. Non-vacuum deposition techniques provide a simple, low-cost alternative. High-quality thin films can be formed by preparing fine powders of precursor materials, depositing thin layers of the particulate precursor materials, and sintering the layers into high-quality, dense films.

Layers of particles can be deposited on large-area substrates with simple non-vacuum techniques such as spraying and printing. Exploratory materials research using simple pneumatic spraying yielded 11.7% cells and 5% monolithic multi-cell modules, but sprayed layers were not very planar (i.e. flat) and not very well packed (i.e. dense), and deposition rates and materials use efficiency were low. The aim of this EISG project was to deposit uniform, planar, well-packed layers with high materials use efficiency.

Project Objectives

The overall aims of this project were to improve particulate layer packing and morphology, and to increase materials use efficiency using advanced spraying techniques. The project explored the feasibility of innovative techniques for depositing planar, well-packed particulate layers at high rates with high materials use efficiency (MUE). The work plan consisted of three objectives:

- Identify, evaluate and procure high-MUE spraying equipment
- Develop high-MUE spraying techniques using CIGS precursor materials
- Fabricate efficient thin-film PV devices using high-MUE techniques

Project Outcomes

High-MUE, non-vacuum deposition techniques were identified and suitable equipment was procured for experimental evaluation

Pneumatic spraying resulted in good atomization and excellent spray directionality, but materials use efficiency was low. Ultrasonic spraying without gas assistance resulted in good atomization, but the lack of carrier gas resulted in poor spray directionality. Gas-assisted ultrasonic spraying yielded good atomization and good spray directionality. Electrostatic spraying at 30 kV yielded relative materials use efficiency gains of 50-65%, but the deposition pattern was erratic and irreproducible. Casting and spray casting yielded high materials use efficiencies and well-packed, planar layers.

High-MUE deposition techniques were developed for depositing layers of CIGS precursor particulate materials

The morphology of particle layers deposited by pneumatic spraying varied with spraying conditions. Layers sprayed in a manner that facilitated rapid local solvent evaporation exhibited microscopically planar surfaces. Layers sprayed using slow solvent evaporation conditions exhibited non-planar surfaces characterized by a network of ridges and valleys. The observed morphological variations were the result of droplet drying mechanisms. Individual droplets of a well-dispersed, well-suspended slurry dry to form rings of particles. Networks of ridges and valleys evolve as particles are differentially collected into ridges by the interplay of ring overlap, particle bounce-back, high-angle overspray, and particle/gas lateral flow. Spray conditions that facilitate rapid solvent drying mitigate local drying effects that cause non-planar layer morphologies; but such conditions reduce materials use efficiency.

Ultrasonic spraying minimizes particle loss mechanisms and yields higher materials use efficiencies; however, ultrasonic spray deposition resulted in non-planar layers characterized by ridges, valleys and small agglomerates. The density of small agglomerates was sharply reduced by spraying under conditions that mitigate in-flight droplet drying, but slow-evaporation conditions aggravated the tendency to form a ridges and valleys topology through cycles of local wetting and drying.

The non-planar morphologies that result from cycles of wetting and drying were circumvented by casting techniques which use a continuous "wet film" of slurry, rather than isolated droplets. The substrate-wide drying front inherent to solvent evaporation from continuous wet films minimized the formation of ridges and valleys.

Efficient thin-film PV devices were fabricated using particulate precursor materials deposited using high-MUE techniques

Cell efficiencies up to 9.4% were achieved during this project. The results demonstrate that high-MUE deposition processes can yield PV device efficiencies needed to fabricate commercially viable products.

Conclusions

The cost-effective formation of high-quality PV films using particle-based, non-vacuum processes requires that one deposit reasonably planar, well-packed layers of particulate precursor materials with high materials use efficiencies. Non-vacuum spraying techniques provide the necessary combination of planar, well-packed layers and efficient materials use provided one mitigates nozzle-related agglomeration, avoids repeated wetting/drying that can cause non-planar morphologies, and facilitates particle rearrangement that can increase packing densities. The demonstration of efficient spray deposition of planar, well-packed layers lays the foundation for the fabrication of efficient, large-area, thin-film PV modules using non-vacuum processes.

Benefits to California

This project demonstrated a better pathway to processing CIGS thin films that can increase the performance, reliability and availability of low-cost photovoltaics by accelerating the commercialization of thin-film CIGS PV technology. PV provides clean, quiet, reliable energy; but is at present too expensive to compete effectively for key high-volume applications. Significant reductions in PV prices require technological advances to reduce manufacturing costs and manufacturing capacity expansions to capture additional economies of scale. The willingness of investors to make the investments necessary to implement new technologies and/or to install additional manufacturing capacity is strongly affected not only by prospects for achieving low costs, but also by the prospects for achieving an attractive overall return on investment.

PV technologies based on thin films hold the low-cost potential to deliver on the enduser pricing reductions necessary to significantly expand the usage of PV, but the commercialization of thin-film PV technologies has been slowed by the difficulty in earning a good return on investment given the costs and complexity of the vacuumbased methods used to deposit the films. This project demonstrated the feasibility of fabricating efficient, thin-film PV by non-vacuum particles-based processes that can deliver both low costs and high returns on investment, and can accelerate the availability of reliable, low-cost PV.

Recommendations

The next steps are to investigate synergies that might arise from combining improved particle layer deposition techniques with improvements to the layer-to-film sintering processes, and to apply the high-MUE particulate layer deposition techniques to the fabrication of large-area, multi-cell modules. Given that the techniques developed in this project can yield higher particle packing densities in particulate precursor layers, improvements to final film quality can accrue from adjustments to the reactive sintering processes used to convert porous precursor layers into dense final films. Given that the techniques developed in this project yield efficient small-area solar cells, it is time to test the techniques to the fabrication of larger-area, monolithically-integrated, multi-cell modules representative of device designs suitable for commercial production.

Abstract

One of the most promising strategies for lowering the cost of photovoltaics (PV) is the use of thin-film technologies in which thin films are formed from particulate precursor materials deposited by non-vacuum techniques. The quality of particle-based PV thin films and in turn the sunlight-to-electricity conversion efficiencies and cost structures of devices based on these films are strongly affected by the planarity and packing density of the layers of particles from which the films are formed and by the materials use efficiency of the processes used to deposit the layers. This report summarizes progress made in depositing planar, well-packed layers of particles using non-vacuum deposition techniques.

Keywords: photovoltaic, PV, solar energy, thin film, CIS, CIGS

Introduction

Background and Overview

Photovoltaics (PV) is a small but rapidly growing sector of California's electrical power generation capacity. PV is used for a wide variety of applications where reliable electrical power is needed. PV is uniquely well-suited for stand-alone applications where electricity is needed far from existing power lines or fuel supplies. PV is increasingly popular in urban applications where clean, quiet, easily-sited electrical power is needed to supplement grid power. Annual worldwide PV sales are approaching \$2 billion dollars with a compound growth rate over the past five years of 30%/yr. California companies produce 15-20% of the world's PV power modules.

In order for PV to significantly impact the State's economy and quality of life, clean PV-generated power must contribute a greater share of the State's power supply. Studies by the Utility PhotoVoltaic Group indicate that the cost of PV must decrease by a factor of 2 - 3 before PV becomes fully competitive for large-scale, grid-connected applications. The levelized cost of PV-generated electricity is dominated by amortization of the up-front capital cost of a PV power system. A prime driver in the cost of PV power systems is the cost of PV power modules. PV modules based on crystalline silicon technologies currently dominate PV markets, but significant cost reductions are difficult with wafer-based technologies due in large part to the underlying cost of silicon wafers.

One of the most promising strategies for lowering PV costs is the use of thin-film technologies in which one dispenses with wafers by instead depositing thin films of materials on inexpensive large-area substrates like window glass. One of the most promising thin-film materials is copper indium gallium selenide (Culn_{1-x}Ga_xSe₂ or CIGS). CIGS PV solar cells have achieved the highest one-sun, terrestrial efficiencies of any thin-film PV technology. Small-area solar cells have been fabricated with efficiencies approaching 19%, and monolithic integrated modules have been fabricated with efficiencies above 14%. In spite of these high efficiencies, commercial production of CIGS PV products has progressed slowly, in large part due to the costs and complexity of the vacuum-based processes typically used to deposit CIGS films.

CIGS films are generally deposited by vacuum-deposition processes such as evaporation and sputtering. To date the best small-area CIGS solar cells were fabricated by vacuum co-evaporation of elements onto heated substrates. Vacuum co-evaporation is a convenient and flexible research process and has yielded sunlight-to-electricity conversion efficiencies near 19%, on small area laboratory samples (e.g. 1 cm²) but it is difficult to deposit films on large areas (e.g. 1,000 - 10,000 cm² for low-cost power modules) with the precision and control necessary to achieve competitive manufacturing costs. Large-area co-evaporation poses difficult challenges, including point and/or line source control and uniformity, materials use efficiency limitations, vacuum system fouling, and film composition control. The convenience and flexibility

that make co-evaporation useful for small-area research make it ill-suited to large-area manufacturing.

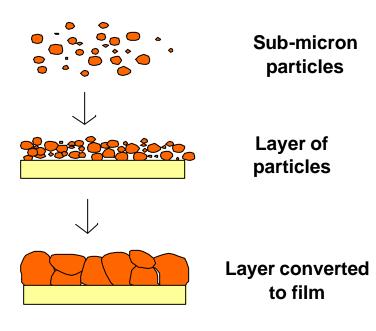
A more manageable method for fabricating large-area CIGS PV films is a multi-step process in which precursor layers (e.g. layers of Cu, In and Ga metal) are deposited and subsequently reacted with additional reactants (e.g. H₂Se gas and/or Se vapor) to form CIGS films. By separating the deposition of critical constituents (i.e. Cu, In and Ga) from the formation of the compound (e.g. addition of Se), multi-step processes simplify the formation of CIGS.

Vacuum-based multi-step processes in which vacuum deposition techniques are used to deposit precursor layers were used to fabricate the most efficient large-area modules reported to date; however, vacuum-based multi-step processes mitigate some of the complications of co-evaporation only at the expense of incurring new complexities. For example, sequential sputtering of metal precursor layers can use magnetron sputtering equipment and techniques developed for the architectural glass coating industry, but CIGS films for solar cells require levels of process stability, film uniformity, in-machine materials inventory, and materials use efficiencies that far exceed typical architectural glass requirements. Though vacuum-based multi-step processes are conceptually easy to implement in high-volume manufacturing, in practice vacuum-based multi-step processes are expensive to implement in large part due to the cost and complexity of vacuum deposition equipment. Relative to the Stages and Gates Process, vacuumbased multi-step thin-film CIGS PV processes are in Stage 3 Research, Stage 4 Technology Development, and early Stage 8 Commercialization at different companies around the world; but commercialization is progressing slowly due in large part to the cost and complexity of the vacuum-based processes.

Non-vacuum deposition techniques provide a simple, low-cost alternative to the complex, capital-intensive vacuum processes. High-quality thin films can be formed by preparing fine powders of precursor materials, depositing thin layers of particulate precursor materials using simple non-vacuum techniques, and converting the layers into high-quality, dense films by reactive sintering in atmospheric-pressure ovens (Figure 1). Non-vacuum deposition of Cu-In-Ga-containing particulate materials is a convenient alternative to using vacuum deposition methods to deposit Cu-In-Ga precursor layers [1]. Particles simplify composition control for multi-component materials such as CIGS since key components can be pre-mixed in the particles in order to simplify composition control during high-speed large-area deposition. By incorporating all of the essential elements in their proper atomic ratios within each mixed-metal particle, variations in precursor layer thickness do not cause variations in CIGS film composition.

Layers of particles can be deposited on large-area substrates with simple non-vacuum techniques such as spraying, printing and spin coating. Spraying techniques are well adapted to uniformly coating large-area substrates for low-cost manufacturing of thin-film PV. Exploratory materials research using simple pneumatic spraying methods yielded 11.7% cells and 5% monolithic multi-cell modules [2,3]. Non-vacuum particles-based processing of CIGS PV is in Stage 3 Research in the Stages and Gates Process.

Fig. 1 Particles to Films



Exploratory materials research also revealed critical challenges to be met to demonstrate the overall feasibility using sprayed particles precursors to PV thin films. For example, while exploratory trials with pneumatic and ultrasonic spraying equipment confirmed that simple slurry spraying techniques could be used to deposit particulate precursor layers, the results were unacceptable in key respects. Sprayed layers were coherent and adherent, but they were not very planar (i.e. flat) and not very well packed (i.e. dense). lt was necessary to deposit relatively thick layers to achieve good coverage. Deposition rates and materials use efficiency were far too low for the process to be economically feasible.

Exploratory research used atmospheric spray deposition techniques characterized by particle packing fractions less than half of the theoretical close-packing of uniform spheres, by layer morphologies with short-range thickness variations of 50% or more, and by materials use efficiencies of less than 25%. Low packing fractions and non-planarity of particulate precursor layers can result in sintered films with low densities and poor transport properties, and can result in low device photovoltages due to excessive junction area and to shunting. The shortcomings of the layer deposition techniques used in the exploratory materials research phase severely eroded the underlying technological and economic advantages of the overall concept.

The challenge addressed in this EISG project was to deposit uniform, planar, well-packed layers with high materials use efficiency. A variety of deposition technologies were conceptually feasible, but the particular constraints of thin-film PV applications limited the workable choices. For example, although it is possible to deposit particulate layers using screen printing, it is difficult to deposit very thin, uniform layers (e.g. 1-2 microns thick without short-range thickness variations due to screen mesh). Similarly, it is difficult to deposit sufficiently thin layers by dip coating or brush coating, and it is difficult to do dip and spin coating of substrates coated with electrode layers that have been patterned to make multi-cell modules. Standard spray painting and standard paint formulations are problematic for thin-film PV use since sprayed paint layers are generally 50-100 thicker than the desired PV precursor layers, and standard paint additives can contribute impurities that would degrade the optoelectronic properties of PV films. This project was directed at demonstrating that advanced spraying techniques could yield the necessary balance of layer properties and deposition parameters.

Project Objectives

The overall aims of this project were to improve particulate layer packing and morphology, and to increase materials use efficiency using advanced spraying techniques. The project explored the feasibility of innovative techniques for depositing planar, well-packed particulate layers at high rates with high materials use efficiency (MUE).

The work plan consisted of three objectives:

- Identify, evaluate and procure high-MUE spraying equipment
- Develop high-MUE spraying techniques using CIGS precursor materials
- Fabricate efficient thin-film PV devices using high-MUE techniques

The first objective was to identify, evaluate and procure technology for depositing planar, well-packed layers of particles with high materials use efficiency. The candidate technologies included low-flow pneumatic spraying, gas-assisted ultrasonic spraying, electrostatic spraying, and the use of slurry additives (e.g. rheology adjusters, flattening agents, etc.).

The second objective was to do bench-scale testing of candidate deposition methods using CIGS precursor materials. The principal goals were to demonstrate short-range thickness uniformity of +/- 10 %, packing density above 40%, and materials use efficiency of at least 85%.

The third objective was to demonstrate the feasibility of the overall particles-to-films concept by fabricating efficient thin-film PV devices using high-MUE techniques. The quantitative goal was to demonstrate 12% cells using high-MUE processes.

The project work plan aimed to demonstrate the feasibility of advanced spraying techniques for depositing planar, well-packed particulate layers at high rates with high materials use efficiency (MUE). The feasibility of high-MUE spraying techniques in turn demonstrates the feasibility of using simple, non-vacuum, particles-based processes for preparing low-cost, thin-film PV.

Report Organization

This Final Report summarizes the approach taken in this project, the experimental results, a discussion of conclusions drawn from the results, and recommendations for future, follow-on work.

Project Approach

This was an experimental project in which scalable processes were tested on a benchscale.

The approach taken for the first objective was to identify, evaluate and procure technology for depositing planar, well-packed layers of particles with high materials use efficiency. The technologies evaluated included low-flow pneumatic spraying, gas-assisted ultrasonic spraying, electrostatic spraying, and slurry additives. The starting point for the first objective was gas-assisted ultrasonic spraying. In exploratory materials trials, pneumatic spraying yielded dense planar layers, but particle capture efficiency was very low; conversely, capture efficiency was high with ultrasonic spraying, but layer morphology was poor. The efficiency of pneumatic spraying was reduced by bounce-back, i.e. particles failing to adhere to the substrate surface in part due to lateral gas flow. The morphology of layers deposited by ultrasonic spraying was hampered in part by in-flight drying of particle-laden slurry droplets and by low droplet momentum. By using a slurry containing low-residue additives that can slow evaporation and aid layer flattening and by using a gas shroud to envelop and direct an ultrasonically-generated aerosol, one could achieve high MUE with good layer morphology.

The first objective also explored alternative high-MUE methods. For example, electrostatic techniques in which a high voltage is applied between the material being sprayed and the substrate being coated can yield coating efficiencies above 95% with both dry particles (e.g. paint powder coating) and slurries (e.g. atomized liquid paints), and spray casting methods can have MUE's near unity. The challenge was to adapt these techniques to the very thin layers needed for PV (e.g. $1\mu m$ thick PV films vs. 50-100 μm thick paint coatings) and to the characteristics of PV precursor slurries (e.g. low solids loading of electrically conductive PV precursor powders versus high solids loading of electrically insulating paint pigments).

The approach taken for the second objective was to do bench-scale testing of deposition methods using CIGS precursor materials. The principal goals were to demonstrate short-range thickness uniformity of +/- 10 %, packing density above 40%, and materials use efficiency of at least 85%.

Short-range thickness uniformity is a measure of the flatness of a layer. While long-range thickness uniformity (e.g. across a 1 cm wide solar cell) is not critical, poor short-range thickness uniformity – i.e. a layer that is non-planar on a micron scale – can decrease the effective density of the final sintered film, increase the effective surface area of the photovoltaic junction, and require thicker precursor layers to assure complete coverage of the underlying electrode. Parameters necessary to achieve good short-range thickness uniformity using high-MUE techniques were experimentally determined.

The packing density of a particulate layer determines how much densification is necessary to achieve a dense final film. While reactive sintering processes densify porous particulate precursor layers, one must achieve a packing density of 20-35% to assure dense final films. A packing density of 55-65% is the maximum possible with uniform solid spheres, but higher densities are theoretically possible with non-uniform particle size distributions.

The materials use efficiency of thin-film deposition processes can have a strong impact on the cost effectiveness of thin-film PV concepts. Sputtering techniques used to deposit precursor layers in vacuum-based multi-step film processes typically have low MUE, e.g. only 25-30% of the target material is sputtered from the target and only 70-80% of the material sputtered from the target is deposited on substrates. Non-vacuum deposition processes can have much higher MUE. For example, while conventional airatomizing spraying has transfer efficiencies as low as 30%, spray casting offers transfer efficiencies near 100%.

The approach taken on the third objective was to demonstrate the feasibility of the overall particles-to-films concept by fabricating thin-film PV devices using high-MUE techniques. Small-area test cells were fabricated to demonstrate materials and photojunction quality.

Project Outcomes

The results and outcomes of the experimental investigation were as follows:

• High-MUE, non-vacuum deposition techniques were identified and suitable equipment was procured for experimental evaluation

The first objective was to identify, evaluate and procure high-MUE spraying equipment. The starting point was pneumatic spraying in an internal atomization spraying configuration. Pneumatic spraying resulted in good atomization and excellent spray directionality, but the large quantities of carrier gas and the high velocity of the atomized droplets resulted in large losses due to bounce back and lateral wind.

Ultrasonic spraying was done using a titanium spray head operating at 40 kHz. Gas-assisted ultrasonic spraying was done with the addition of a concentric gas shroud to the ultrasonic spraying assembly. Ultrasonic spraying without gas assistance resulted in good atomization, but the lack of carrier gas resulted in poor spray directionality. Spray coverage and uniformity was strongly affected by air currents. Gas-assisted ultrasonic spraying yielded better spray directionality relative to unassisted spraying.

Electrostatic spraying was done using a pneumatic sprayer set at 30 kV positive potential relative to a grounded substrate. Early tests of electrostatic spraying yielded

relative materials use efficiency gains of 50-65%, but the deposition pattern was erratic and irreproducible. The balance of the experimental work focused on gas-assisted ultrasonic spraying and on spray casting.

Casting and spray casting was done with higher slurry solids loading to facilitate deposition of particulate layers using lower slurry volumes. Casting was done using an eyedropper. Spray casting was done using the gas-assisted ultrasonic spraying equipment.

High-MUE deposition techniques were developed for depositing layers of CIGS precursor particulate materials

The second objective was to develop high-MUE techniques for depositing nanoparticulate CIGS precursor materials. This objective was addressed by depositing particulate layers with various spray and casting techniques.

Cu-In-Ga oxide precursor materials were prepared as solid, spherical, sub-micron particles. Slurries of suspended precursor particles were prepared by dispersing particles in common solvents. Layers of particles were spray deposited on bare and molybdenum-coated soda-lime glass substrates. Precursor layers were densified into CIGS films by atmospheric pressure, reactive sintering with Se-containing reactants at 400-600°C. Particulate layers were spray deposited using pneumatic, ultrasonic and gas-assisted ultrasonic spraying. In all cases, spraying was done downward onto substrates resting on a Kapton heater mounted on an x-y raster table.

Layers and films were characterized by precision weight measurements and by optical and scanning electron microscopy. The quantity of material deposited was estimated by weight gain per unit area. Layer thickness was measured by scribing the layer with a mechanical stylus and measuring the difference between high-magnification optical microscope focal planes of the substrate and the average layer surface using a high-precision z-axis micrometer. Layer planarity was similarly estimated using optical microscopy by measuring the height difference between the highest peaks and the lowest near-by valleys. Pinholes were mapped using bright-field reflected light for Mocoated substrates and transmitted light for bare glass substrates. Average packing densities of layers of particles were calculated from the ratio of the weight gain per unit area divided by the product of layer thickness and estimated solid density of the precursor material.

The surface morphologies and densities of CIGS PV films prepared by reactive sintering of layers of Cu-In-Ga oxide particulate precursor materials are strongly affected by the morphologies and densities of the precursor layers [4]. Sprayed particulate layers are adherent (i.e., layers of particles adhere well to the underlying substrate), coherent (i.e., particle-to-particle cohesion is sufficient to form a stable layer), conformal (e.g., sprayed layers conformally overcoat Mo patterned to formed monolithic multi-cell modules), and typically have a macroscopically uniform matte appearance. However, the microscopic

morphology and the materials use efficiency (i.e. the percentage of sprayed particles that are incorporated into the layer on the target region of the substrate) of sprayed particle layers can vary considerably depending on spraying conditions.

Pneumatic spraying can yield planar layers, but early efforts to deposit layers of particles by pneumatic spraying were plagued by high areal densities of large agglomerates (Figure 2). The agglomerates were 25-75 μ m in diameter and 30-40 μ m in height, more than sufficient to cause electrical shunting by disrupting the p-n junction of a CIGS film with a target thickness of ca. 3 μ m. Given estimated spray droplet sizes and target slurry solids loading, these large agglomerates are about 1000 times larger in volume than agglomerates that might be expected to be formed by in-flight drying of an average slurry droplet. Initially it was theorized that these large agglomerations were related to accumulation phenomena (e.g. accumulation of particles moving laterally due to spraying carrier gas flow), but experiments linked these features to agglomeration in and/or on the spray nozzle itself. Process and hardware changes that mitigate nozzle-related agglomeration reduced the areal density of large features from 500-1000 cm⁻² to less than 10 cm⁻².

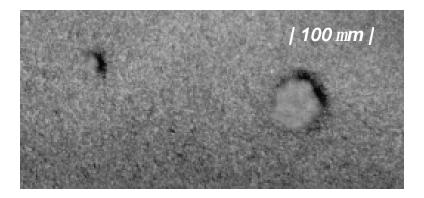
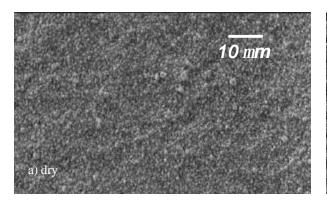


Figure 2. Optical micrograph of pneumatically-sprayed layer with large agglomerates.

The morphology of particle layers deposited by pneumatic spraying varies considerably with spraying conditions. Layers sprayed in a manner that facilitates rapid local solvent evaporation (e.g. high-volatility solvents, high substrate surface temperatures, high carrier gas flows, low slurry spray rates, etc.) generally exhibited microscopically planar surfaces (Figure 3a). The depth of surface features on such layers was typically less than a third of the average thickness of the overall layer, and the average packing density of the particles within a layer was 25-40%. Layers sprayed using slow solvent evaporation conditions (e.g. low-volatility solvents, low substrate surface temperatures, low carrier gas flows, high slurry spray rates, etc.) often exhibited non-planar surfaces characterized by a network of ridges and valleys (Figure 3b). The network of ridges and valleys can yield short-range thickness variations comparable to the average thickness of the layer, hence average packing densities were only 15-20% and areas of the underlying Mo electrode were exposed and caused electrical shunting.



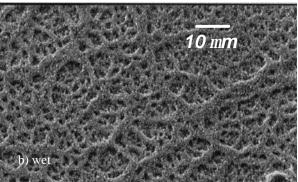


Figure 3. Optical micrographs of pneumatic sprayed layers using a) "dry" and b) "wet" conditions.

The observed morphological variations in pneumatically sprayed particle layers are likely related to mechanisms described by Nagel and colleagues at the University of Chicago to explain the formation of coffee stains [5]. For an individual droplet of a welldispersed, well-suspended slurry (e.g. a drop of coffee beverage), Nagel found that rings of particles are formed when substrate surface roughness pins the edge of the drop so that the area does not decrease as the solvent evaporates and so that suspended particles are transported to the perimeter due to differentially higher solvent evaporation rates at the drop edges. Experiments with Cu-In-Ga oxide particles sprayed onto Mo show rings of particles where isolated droplets dry in a manner similar to Nagel's coffee drops. Networks of ridges and valleys as seen with pneumatic spraying under "wet" conditions evolve as particles are differentially collected into ridges by the interplay of ring overlap, particle bounce-back, high-angle overspray, and particle/gas lateral flow. Ridge/valley formation can be mitigated by controlling local wetting and drying fronts on the just-sprayed slurry coating. Spray conditions that facilitate rapid solvent drying (e.g. higher carrier gas flow rates) can mitigate local drying effects that cause non-planar layer morphologies; but such conditions reduce materials use efficiency (e.g. higher carrier gas flows increase particle loss by bounce-back and lateral gas flow).

Ultrasonic spraying can minimize particle loss mechanisms and yield high materials use efficiencies (e.g. MUE's > 85%). Ultrasonic sprayers mechanically atomize liquid without the shearing forces of a carrier gas, thus ultrasonic spraying can deposit slurry coatings with minimal materials losses due to bounce-back and overspray. Without a carrier gas, an ultrasonically-formed aerosol drifts erratically; the use of a gas shroud to envelop the aerosol can improve the directionality of deposition. Early tests with ultrasonic spray deposition of metal oxide precursors for PV films resulted in non-planar layers characterized by ridges, valleys and small agglomerates (Figure 4). Unlike the large agglomerates evident on early pneumatic layers, the small agglomerates evident on ultrasonically-sprayed layers are comparable to those anticipated from in-flight drying of individual slurry droplets. Experiments with spray conditions indicate that the underlying ridge/valley structure is closely related to the structure of pneumatically-sprayed layers

deposited under "wet" conditions. The density of small agglomerates can be sharply reduced by spraying under conditions that mitigate in-flight droplet drying (e.g. low-volatility slurry solvents), but slow-evaporation conditions aggravate the tendency to form a ridges and valleys topology through cycles of local wetting and drying.

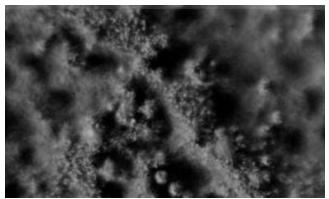
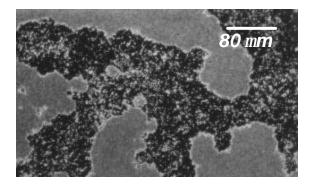


Figure 4. Optical micrograph of ultrasonically-sprayed layer of particles.

The non-planar morphologies that result from cycles of wetting and drying can be circumvented by casting and printing techniques where particle layers are formed from a single slurry coating. Casting and printing techniques utilize a continuous "wet film" of slurry, rather than isolated droplets; and solvent evaporation from such continuous wet films typically occurs along a substrate-wide drying front rather on a droplet-by-droplet basis, thus the formation of ridges and valleys is minimized. However, these potential advantages of casting and printing require that the slurry be well-dispersed and well-suspended and be able to uniformly wet the substrate surface. Low-residue dispersants aid in stable suspension of the precursor particles in the solvent. Wetting agents and substrate surface cleanliness aid in ready coating of the slurry onto the substrate. Poorly dispersed slurries and/or poor substrate wetting result in non-uniform, non-planar layers (Figure 5).



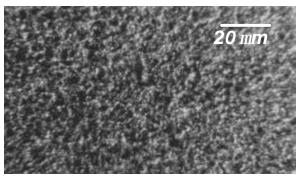


Figure 5. Optical micrographs of layers cast using a) poorly dispersed and b) well dispersed slurries.

Casting techniques also provide advantages in layer packing and in materials use efficiency. Given that casting facilitates particle rearrangement during comparatively slow solvent evaporation, casting can yield particle layers with higher packing densities; average packing densities of 40-55% are measured. Given that casting involves broadcasting a slurry in a manner that minimizes bounce-back and overspray, materials use efficiencies can be high; materials use efficiencies above 85% are typical with spray casting.

By applying the improvements described above to deposit more planar, better packed layers of precursor particles, the density of sintered CIGS films was increased (Figure 6).

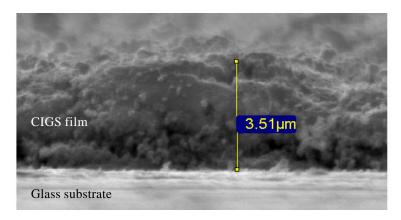


Figure 6. Cross-sectional electron micrograph of a particles-based CIGS PV device.

• Efficient thin-film PV devices were fabricated using particulate precursor materials deposited using high-MUE techniques

The third objective was to fabricate efficient thin-film PV devices using high-MUE techniques. This objective focused on using small-area solar cell devices as a test bed to demonstrate the impact of the high-MUE layer deposition techniques. Cell efficiencies up to 9.4% were achieved during this project. While these efficiencies were less than those originally targeted, the shortfall likely reflected the impact of processing variables (e.g. substrate effects) outside of the scope of this project. The results demonstrated that high-MUE deposition processes can yield PV device efficiencies need to fabricate commercially viable products.

Conclusions and Recommendations

Conclusions

The formation of high-quality PV films using particle-based, non-vacuum processes requires that one deposit reasonably planar, well-packed layers of particulate precursor materials. For a thin-film PV process to fully realize the low manufacturing cost potential inherent in utilizing thin films of PV materials in lieu of wafers of PV materials, films must be deposited with high materials use efficiencies. Non-vacuum spraying techniques can provide the necessary combination of planar, well-packed layers and efficient materials use provided the processes are tuned to mitigate nozzle-related agglomeration, to avoid repeated wetting/drying that can cause non-planar morphologies, and to facilitate particle rearrangement that can increase packing densities. The demonstration of efficient spray deposition of planar, well-packed layers lays the foundation for the fabrication of efficient, large-area, thin-film PV modules using non-vacuum processes.

Recommendations

The recommended next steps in developing this technology are to investigate synergies that might arise from combining these improved particle layer deposition techniques with improvements to the layer-to-film sintering processes, and to apply the high-MUE particulate layer deposition techniques to the fabrication of large-area, multi-cell modules. Given that the techniques developed in this project can yield higher particle packing densities in particulate precursor layers, improvements to final film quality (e.g. larger grain sizes, better electro-optical properties, etc.) might accrue from adjustments to the reactive sintering processes used to convert porous precursor layers into dense final films. Given that the techniques developed in this project yield efficient small-area solar cells, it is appropriate to next apply the techniques to the fabrication of larger-area, monolithically-integrated, multi-cell modules representative of device designs suitable for commercial production.

Commercialization Potential

The fabrication of low-cost, high-performance PV modules using thin films deposited using particle-based, non-vacuum processes has excellent potential for commercial success. Two of the world's largest manufacturers of PV modules have indicated an interest in licensing the technology. The gating milestones for pilot production are to demonstrate that efficient, large-area, multi-cell monolithic modules can be fabricated, and to do field testing on prototype products. These Stage 4 and 5 milestones are well-matched to follow-on projects under the Public Interest Energy Research (PIER) program.

Benefits to California

This project aimed to increase the performance, reliability and availability of low-cost photovoltaics by accelerating the commercialization of thin-film CIGS PV technology by demonstrating a better pathway to processing CIGS thin films.

Photovoltaics provides clean, quiet, reliable energy; but PV is at present too expensive to compete effectively for key high-volume applications. PV demand – hence PV's positive impact on the State's economy and quality of life – will increase as the price of PV decreases. Significant reductions in PV prices require technological advances to reduce manufacturing costs and manufacturing capacity expansions to capture additional economies of scale. The willingness of investors to make the investments necessary to implement new technologies and/or to install additional manufacturing capacity is strongly affected not only by prospects for achieving low costs, but also by the prospects for achieving an attractive overall return on investment.

PV technologies based on crystalline silicon dominate the present PV market, but the cost of silicon wafers largely precludes the price reductions needed for PV to become a major energy resource for California. PV technologies based on thin films hold the low-cost potential to deliver on the 2-3 x end-user pricing reductions necessary to significantly expand the usage of PV, but the commercialization of thin-film PV technologies has been slowed by the difficulty in earning a good return on investment given the costs and complexity of the vacuum-based methods used to deposit the films.

This project demonstrates the feasibility of fabricating efficient, thin-film PV by non-vacuum particles-based processes that can deliver both low costs and high returns on investment, and can accelerate the availability of reliable, low-cost PV. Net manufacturing cost reductions of ca. 50% are projected relative to competing PV technologies. The projected cost reductions of thin-film CIGS relative to wafer-based PV technologies total 50% and are concentrated in direct materials and labor. The projected cost reductions of non-vacuum CIGS processes relative to vacuum-based CIGS processes total ca. 45% and are concentrated in capital equipment costs.

California will garner several benefits from cost-effective PV technology. In the near-term the State's balance of trade is helped by the export of PV products. In the longer-term the State's security (e.g. stability of energy supply), prosperity (e.g. balance of trade losses for imported oil) and quality of life (e.g. environmental quality) will benefit from low-cost photovoltaics as one facet of a sustainable energy portfolio.

Development Stage Assessment

The overall development of non-vacuum techniques for fabricating efficient CIGS photovoltaic power modules is progressing through Stage 3: Research. The advancements made during the course of this EISG project provide a proof of feasibility (i.e. meet the criteria of Gate 3) for one of the primary elements of the target non-vacuum technologies. The current status is summarized in the Project Development Stage Activity Matrix table below and discussed for specific activity sectors in the accompanying comments.

Table 1. Project Development Stage Activity Matrix

Stages Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop- ment	5 Product Develop- ment	6 Demon- stration	7 Market Transfor- mation	8 Commer- cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The use of non-vacuum techniques for using particulate precursor materials to form high-quality CIGS films for incorporation into efficient thin-film photovoltaic power modules involves three elements: 1. preparation of suitable particulate precursor materials, 2. deposition of layers of particles, and 3. sintering of layers of particles into high-quality CIGS films. Prior research funded in part by grants from the U.S. Department of Energy under its Small Business Innovation Research (SBIR) program established the preliminary feasibility of all of the elements, and highlighted the second element - deposition of layers of particles - as a gating factor in the overall proof of feasibility of the technology. This project focused on depositing layers of particles, in particular in demonstrating methods of depositing planar, well-packed layers of particles with high materials use efficiencies. The results of this project position the technology to advance to the next stages. The status of technology relative the seven concurrent activities of the Stages and Gates Process is summarized below.

Marketing / Connection to the Market

Prior to this project, studies were undertaken to define end user market needs (e.g. PV module performance and price targets, product features relative to specific field applications, etc.), to evaluate existing and anticipated competing technologies, and to define a technology development / market entry pathway. Briefly summarized, these studies indicated that California ratepayers would benefit from lower costs for PVgenerated electricity, that lower PV power module costs were a key driver in reducing PV-generated electricity costs, that module cost reductions of 50-65% would sharply increase the size and scope of PV applications in California, and that thin-film CIGS PV power modules could yield the desired cost reductions if efficient, non-vacuum processing techniques could be developed and commercialized. Present and prospective users of PV products were surveyed to determine market size, customer needs, market segmentation and current/future competitive products. Survey results were consistent with independent studies done by utility groups which concluded that significant demand would emerge - in particular for grid-connected, urban-sited power if PV system prices could be reduced by a factor of 2-3. Analyses of likely commercialization pathways underscored that the most likely pathway to rapid, largescale commercialization was by developing and licensing technology to larger, wellcapitalized market players. Meetings with potential licensees revealed specific technology development criteria necessary to attract technology development funding / licensing agreements. The technical focus of this EISG project was on those criteria.

Engineering / Technical

Prior to this project, the basic non-vacuum processing concept was defined, the state of the art was investigated, detailed product and process specifications were drafted, a team of materials science professionals was assembled, and candidate component technologies were identified. During the SBIR-funded exploratory research, candidate component technologies (e.g. how to prepare suitable particulate precursor materials, how b prepare suitable sprayable slurries, etc.) were tested on a bench scale, and preliminary experimental results were used to refine process designs and cost projections and to make a preliminary assessment of manufacturability. During this EISG project, the focus was on testing gating improvements to a key processing step, namely the deposition of layers of particles. The target criteria (e.g. planarity, packing density and materials use efficiency) for the step were achieved.

Legal / Contractual

Prior to this project, intellectual property was defined, prior art was reviewed, patent applications were submitted, and technology licensing requirements were assessed. It was determined that no barriers to development existed and that sustainable competitive advantages could be secured. Work environments and activities were structured to minimize regulatory and permitting requirements. During this EISG project notice of allowance for the first patent was received.

Environmental, Safety, Risk & Quality Plans

Prior to this project, the contractor used its experience as a consultant to the U.S. Department of Energy's environmental, safety and health (ES&H) initiative for photovoltaics managed by Brookhaven National Laboratory to assess ES&H issues vis-à-vis the targeted technology in both the research and commercialization phases. Self-imposed, voluntary guidelines (e.g. no use of compressed toxic gases) were defined to mitigate EH&S risks.

Prior to this project, market and commercialization risks were identified and prioritized, and preliminary steps taken to mitigate those risks. For example, the integrated cost projections of initial commercialization were made, potential financing barriers were identified (e.g. capital costs of substrate processing equipment), and risk mitigation options were identified (e.g. outsourcing of substrates).

Prior to this project, quality controls were instituted. Computerized "Design of Experiments" techniques and "Statistical Process Control" data analyses were implemented to assure experiment reproducibility and control.

During this EISG project previously identified plans for environmental, safety, risk and quality control were followed. The results of this project were consistent with prior plans.

Strategic

In preparing a proposal to the EISG program, it was confirmed that the concept investigated in this EISG project fit within the PIER Program objectives and goals within the Renewables sector. The PV technology that was the focus of this EISG project can complement and leverage related distributed generation technologies in delivering to ratepayers a cost-effective, broadly-based, reliable supply of electricity.

Production Readiness / Commercialization

Prior to this project, the prospects and projected timeline for commercialization were analyzed, and the resources and likely participants for commercialization were identified. Potential commercialization partners were identified and introductory meetings were held to assess potential partners' interest in the subject technology. Investment criteria (e.g. projected product cost, projected capital investment, projected return on investment, etc.) were identified and used to define into research priorities. This EISG project addressed one of the key gating factors identified by these meetings with potential commercialization partners.

Public Benefits / Costs

This EISG project provided significant potential public benefits at modest public cost. The PV industry in California has an annual revenue flow of ca. \$200 million. The technologies that were the focus of this project hold the promise of cutting manufacturing costs by 50% or more, and utility studies suggest that cost reductions of that magnitude could exponentially increase PV sales. While the technologies developed under this EISG project would likely by commercialized by private-sector companies, ratepayers and taxpayers would benefit financially by the availability of lower-cost, stable-price PV-generated electricity. PV provides zero-emissions, low-noise distributed power that can be easily sited in both rural and urban areas. PV output power profiles closely match urban demand profiles, enhancing the value of PV-generated power. This EISG project focused on improvements in depositing layers from which PV films were formed; the potential benefits of commercializing this technology warrant follow-on work on related research issues (e.g. advanced sintering techniques) and on technology development issues (e.g. scale-up to larger substrate sizes).

References

- 1. C. Eberspacher, K. Pauls and C. Fredric, "Improved Processes for Forming CuInSe₂ Films," 2nd World Conf. PV Solar Energy Conv., Vienna, July 1998, pp. 303-306.
- 2. C. Eberspacher, C. Fredric, K. Pauls and J. Serra, "Thin-film CIS Alloy PV Materials Fabricated Using Non-vacuum, Particles-based Techniques," European Materials Research Society Meeting, Strasbourg, June 2000.
- 3. C. Eberspacher, C. Fredric, K. Pauls and J. Serra, "Thin-film CIGS PV Modules Fabricated Using Simple Non-vacuum Techniques," 16th EC-PV Solar Energy Conf., Glasgow, May 2000, pp. 710-713.
- C. Eberspacher, K. Pauls and J. Serra, "Non-vacuum Techniques for Fabricating Thin-film CIGS," 26th IEEE Photovoltaic Specialists Conference, Anchorage, 2000, pp. 517-520.
- 5. R. Deegan, O. Bakajin, T. Dupont, G. Huber, S. Nagel and T. Witten, *Nature* 389, 827, 1997.

Glossary

Acronyms used in this report include:

PV = photovoltaics DOE = U.S. Department of Energy

CIS = CuInSe₂ SBIR = Small Business Innovation Research

 $CIGS = Culn_{1-x}Ga_xSe_2$ MUE = materials use efficiency

NREL = National Renewable Energy Laboratory

PIER = Public Interest Energy Research

List of Figures

- 1. Particles to Films diagram
- 2. Optical micrograph of pneumatically-sprayed layer with large agglomerates.
- 3. Optical micrographs of pneumatic sprayed layers using a) "dry" and b) "wet" conditions.
- 4. Optical micrograph of ultrasonically-sprayed layer of particles.
- 5. Optical micrographs of layers cast using a) poorly dispersed and b) well dispersed slurries.
- 6. Cross-sectional electron micrograph of a particles-based CIGS PV device.

List of Tables

1. Project Development Stage Activity Matrix